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**A SYSTEM USING SOLID CERAMIC OXYGEN ELECTROLYTE CELLS
TO MEASURE OXYGEN FUGACITIES IN GAS-MIXING SYSTEMS**

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A SYSTEM USING SOLID CERAMIC OXYGEN ELECTROLYTE CELLS TO MEASURE OXYGEN FUGACITIES IN GAS-MIXING SYSTEMS

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SUMMARY

A system that uses a calcia stabilized zirconia ceramic electrolyte oxygen concentration cell to continuously monitor the oxygen fugacity in a vertical-quench furnace has been designed, built, and tested. The construction makes extensive use of O-ring seals, commercial tube fittings, and simple solid-state electronic control and measuring devices.

Descriptions are given of a furnace using fibrous zirconium oxide superinsulation and molybdenum disilicide heating elements; a gas mixer using multiturn needle valves and a special gas-mixing chamber; the devices to monitor the electromotive-force output of the electrolyte cell; the devices to produce programed rates of change of temperature and redox conditions; the techniques for preparation, mounting, and experimenting with various samples; the operation and maintenance of the system; and the calibration of the system. This system is durable, highly accurate, and relatively inexpensive to construct. Because the redox conditions are measured directly, the system can be operated under conditions not possible in classical gas-mixing systems.

INTRODUCTION

Control and measurement of oxygen fugacity is essential in the study of many geological, chemical, and metallurgical problems. A method to control oxygen fugacity at 101.3 kN/m^2 (1 atmosphere) pressure is gaseous buffering, or gas mixing. An extensive discussion of this technique is given in references 1 and 2. Briefly, two gases that undergo reactions to produce oxygen (such as carbon dioxide and carbon monoxide or hydrogen and carbon dioxide) are accurately mixed and flowed over a sample in a furnace. Oxygen fugacities between 10^{-24} and 10^{-3} , depending on the temperature and gases, can easily be produced. As usually used, this technique assumes equilibrium among the gaseous species involved in order to compute the oxygen fugacity (ref. 3); however, some investigators (refs. 4 and 5) have suggested that the gas reactions may not come to equilibrium, and thus the oxygen fugacities during an experiment may not be the same as those computed for the

*Lockheed Electronics Corporation.

gaseous mixture. Fortunately, certain solid ceramic electrolytes can be made into oxygen concentration cells that directly measure the oxygen fugacity in the gas-mixing furnace system.

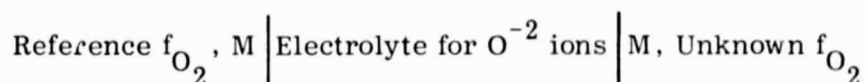
Solid ceramic oxygen electrolyte cells have been used extensively in NASA Lyndon B. Johnson Space Center (JSC) studies involving thermodynamics (ref. 6), phase equilibria (ref. 7), and dynamic systems (ref. 5); therefore, techniques and hardware were developed to permit such studies to be conducted on a routine basis. This experience should be useful to other investigators who desire to undertake gas-mixing studies. The objective of this report is to describe the experimental system and operating procedures; the report also supplements, expands, and corrects the earlier work described in references 8 to 10.

The authors gratefully acknowledge the contributions and significant suggestions of their JSC coworkers including Dr. G. E. Lofgren, Dr. T. M. Usselman, Dr. Richard V. Morris, Dr. C. Donaldson, D. Smith, and E. Quinn.

As an aid to the reader, where necessary the original units of measure have been converted to the equivalent value in the Système International d'Unités (SI). The SI units are written first, and the original units are written parenthetically thereafter.

THEORETICAL CONSIDERATIONS

Various ceramics may be used to construct electrochemical cells. Reference 11 contains a list of these materials and an extensive discussion of their behavior, in terms of both the theoretical and practical details of their functioning. This reference is a basic source for access to the literature on electrochemical cells of this type. For this report, it is sufficient to point out that, schematically, the cell is arranged as follows:



where f_{O_2} is the fugacity of oxygen and M represents the conducting contacts.

The net reaction at the cell is $\text{O}_2 + 4\text{e}^- = 2\text{O}^{-2}$ and thus the voltage across the cell is given by

$$E = \frac{RT}{4F} \ln \frac{f_{\text{O}_2(\text{unk})}}{f_{\text{O}_2(\text{ref})}} \quad (1)$$

where E is the voltage, R is the universal gas constant, T is the temperature in kelvin, F is the Faraday constant, and the subscripts (ref) and (unk) are

reference and unknown, respectively. With pure oxygen as a reference gas, the equation may be reduced to

$$\log f_{O_2} = \frac{20.159}{T} E \quad (2)$$

where T is in kelvin and E is in millivolts.

The ceramic electrolyte used at JSC is zirconia-calcia ($(ZrO_2)_{0.85}(CaO)_{0.15}$) ceramic. The lower response limit for the zirconia-calcia ceramic is given by

$$\log f_{O_2} = -\frac{60\,500}{T} + 23.5 \quad (3)$$

There is no sharp change in the behavior of the ceramic electrolytes when their response limit is exceeded. Beyond the regions of correct response, the electromotive force (emf) of the cell reflects conduction mechanisms other than those specified in equations (1) to (3). Consequently, if these cells are used under conditions different from those for which confirmed results have been obtained, care must be taken that the electromotive forces obtained are externally and internally consistent. The cells function properly above 873 K (600° C) and within their range of operation, and experience has shown that any irregularities are due to some source of error other than the cells.

SYSTEM DESCRIPTION

The complete system for control and manipulation of oxygen fugacity is illustrated by the block diagram in figure 1. The system has the capability of controlling temperature and oxygen fugacity, of independently and automatically varying temperature and oxygen fugacity during experiments, and of recording both temperature and oxygen fugacity as a function of time. If the researcher's goals are more limited, the system can be simplified. The following subsections give brief descriptions of the construction and operation of the various components of the system.

Furnace

Rather than a platinum-wound furnace, furnaces with hairpin molybdenum disilicide heating elements are used. These heating elements are much less expensive than precious metal wire, are useful to much higher process temperatures (furnace used routinely at 1848 K (1575° C)), and have nominal lifetime in excess of 18 months. Particularly when used with the new zirconia-based insulations, these elements can be made into lightweight, rugged, high-temperature furnaces.

A diagram of such a furnace is shown in figure 2. The radially symmetrical distribution of the hairpin heating elements about the muffle tube produces a large, uniform hot spot (fig. 3). Electrical shielding of the electrode is unnecessary in this system.

Temperature Control

The furnace elements are the low-resistance type, and a matching transformer is needed. Consequently, the type of temperature controller must be compatible with inductive loading. Although it is possible to build such control systems, commercial systems are preferable. (Complete furnaces with compatible temperature control systems are available commercially from several sources.)

Temperature Programing

Because two thermocouples, one to control the furnace and another to measure the process, are used, a simple method of temperature programing can be used. The method developed at JSC consists of adding or subtracting a controlled voltage to the furnace control thermocouple. Figure 4(a) is a block diagram illustrating the wiring for a temperature programing system, and figure 4(b) is a schematic for a motor-driven stabilized millivoltage source. If the wiper arm of the output potentiometer is motor driven, a controlled, time-varying millivoltage signal is generated that may be used to produce various temperature increases or decreases. The magnitude of the desired temperature is fixed by setting the total voltage drop across the potentiometer, or portion thereof, to be equal to the equivalent millivoltage change of the control thermocouple; the time base is set with gears or variable speed motors. (Chart drive motors are excellent for use in these systems.)

The potentiometer should have as small a total resistance as is reasonable (a 10-turn, 1000-ohm potentiometer functions well) to eliminate nonlinearity effects of the potentiometer and to prevent loading of the temperature controller input. Logarithmic and exponential patterns of temperature change may be produced by using precision audio taper potentiometers rather than linear taper potentiometers. If complete freedom of control is desired, a commercial programmer may be utilized by using the "set point potentiometer" of the programmer as the potentiometer in the multivoltage source.

Furnace Heads

To maintain the controlled gas atmosphere in the furnace, gas-tight seals (heads) are provided. Because of the high process temperatures, these heads are water cooled. Figures 5 to 7 illustrate the construction and use of these heads. Details of the end plates are not shown because they may be modified by the individual investigator. Although not obvious in the figures, the O-ring grooves should be cut so that all metal parts can be brought into tight contact with each other to increase the efficiency of the water cooling. Because ceramic tubes vary in size, precise matching instructions cannot be given.

These heads have been successfully used on 3.8- and 6.4-centimeter (1.5 and 2.5 inch) bore systems. However, in the 6.4-centimeter (2.5 inch) bore design, radiative transfer to the heads is sufficient to warrant incorporation of a second cooling ring, particularly at the top of the furnace (fig. 8).

The heads should be connected for series waterflow and the waterflow should be directed from top to bottom. Interlocks should also be provided to turn off the furnace power in the event of a loss of coolant flow.

Gas Mixers

The construction of a manual gas mixer is shown in figure 9. The mixer is constructed with hard tubing using appropriate tube fittings. The operation of such a gas mixer is rather straightforward; the only precaution is that adjustment of the gas-mixing ratio must be accomplished by simultaneously decreasing one gas flow while increasing the other so that total flow through the furnace always remains constant. Low-pressure gas regulators are used between the two-stage regulators on the gas cylinders and the gas mixer. This is not essential if only one furnace is to be used with a set of gas cylinders; however, if several gas mixers are operated off the same cylinders, low-pressure regulators must be used on all gas mixers to prevent the interaction of the flows.

Figure 10 illustrates the construction of a mixing chamber that significantly improves the stability of the system. It is convenient to mount the device directly on the gas input to the furnace, because changes in mixing ratio are communicated to the hot zone more rapidly than if a remote mixing chamber is used. This mixing chamber is useful in those cases in which one of the gases is in lower concentration than the other. If the minor component is fed through the small-diameter inner tube (fig. 10), the flow of the major component will not affect the flow of the minor component as much as when simple mixing chambers are used. This mixing procedure is particularly recommended when using automatic gas mixing systems, which are described later in this report.

Electrolyte Cell

The construction and mounting of the electrolyte cell are illustrated in figure 11. O-ring seals are used to produce gas-tight seals against the ceramic while permitting enough slippage to accommodate the differential expansion of the components during heating. There are two ways of mounting the assembly in the furnace. The system at JSC is mounted so that the sensing head of the electrode and the sample are symmetrically disposed about the axis of the furnace; however, in small-bore systems, a coaxial arrangement is necessary. The coaxial design precludes vertical quenching.

Several points relevant to the construction of the cell are not obvious from figure 11. Inner and outer electrode contacts are easily made from metal tubing that is made to fit the ceramic tube. Lead wires are spotwelded to the contacts. The contacts and leads may be made of any metal that does not react with the ceramic. However, both inner and outer contacts and leads should be of the same metal.

One leg the thermocouple may be used as the reference lead for the cell because it simplifies wiring and permits the use of heavier lead wires. Heavy lead wires (0.76 centimeter (0.30 inch)) and contacts (0.6102 centimeter (0.004 inch)) extend the cell lifetime. The process measuring thermocouple is inside the cell and protected from adverse effects of the furnace gas; but, because of this isolation from the furnace atmosphere, the system must be carefully calibrated under actual process conditions to ensure that the measured temperature and oxygen fugacity are the same as those experienced by the sample. If this common lead technique is used, care must be taken not to create a ground loop between the oxygen fugacity measuring system and the temperature measuring system.

The reference of the cell is provided by an oxygen gas purge in the interior of the cell. This flow should be delivered to the inner sensing head; therefore, the inner ceramic tube that supports the leads and inner contact must be continuous.

Flow rates of 0.00085 to 0.0017 stdm³/hr (0.03 to 0.06 stdft³/hr) are sufficient to provide a stable reference. Oxygen is vented to the laboratory from the base of the cell through the holes carrying the lead wires out of the cell.

The electrode is introduced from the bottom of the furnace and the atmosphere-control gas flow is directed from top to bottom. This procedure provides a stable operation; any volatiles that condense on the cell (water from hydrogen-containing mixtures) will flow to the bottom of the furnace, and any leaks of reference gas from the cell will be flushed out of the system without affecting the charge.

The electrolyte ceramic cells are available in several sizes. Those of 0.635 centimeter (0.25 inch) outside diameter (OD) and 0.953 centimeter (0.375 inch) OD were used in the system described here. The larger tubes are preferred because they are less sensitive to thermal and mechanical shock.

Electrode Measurement System

Figure 12(a) is a schematic of the high input impedance millivoltmeter that is used to measure the output of the electrolyte cell. The measurement is made by comparing the cell output to the calibrated and stable millivoltage power supply in the meter. The zero-gain amplifiers on the front end of the device provide isolation. Integrated circuit (IC) 1A and IC1B provide the high impedance input necessary for proper cell loading. When used as a null meter, the positive input should be grounded and the negative cell input connected to pin 4 on the printed circuit board (fig. 12(b)). The IC2 provides recorder output drive for the 10-kilohm potentiometer connected to pin 15 of the circuit board. The 10-kilohm potentiometer connected to pin 17 gives deviation-from-null output for a recorder; IC4 couples the reference voltage from the null potentiometer connected between pins 14 and 8 on the circuit board with IC3. Power is supplied by the transformer/diode/regulator network shown (output is about 12 V dc); this part of the circuit is the same as that shown in figure 4(b) for the temperature programmer.

Calibration and adjustment of the meter is straightforward. Two outputs are provided: one gives deviation from set points; the other, output from the cell. These outputs may be used to display emf graphically or to drive feedback circuitry for automated control of oxygen fugacity. (See the note on fig. 12(a) and the section entitled "Automated and Programmable Redox Control.")

The device is rugged, inexpensive, and stable; however, it was not designed to replace instrumentation requiring microvolt resolution, et cetera. It is easily calibrated to be accurate to ± 1 millivolt, a feature that is more than sufficient for use with the cells. The device automatically performs time averaging of the emf input. It is not as badly affected by transients as are more complex instruments and is thus capable of functioning with less electrical shielding.

The electrolyte cell is a high impedance device at low temperature ($\approx 10^{14}$ ohms at 873 K (600° C)); but, at high temperature, its impedance decreases rapidly to a few thousand ohms at 1753 K (1500° C). At high temperature, it is inherently less susceptible to interference and impedance mismatches. Above 1473 K (1200° C), its output has been measured with a normal volt-ohm-meter. The system used gives accurate results between 973 and 1873 K (700° and 1600° C).

Automated and Programmable Redox Control

Because the redox state in the furnace is directly monitored as an emf output from the cell, the output is adaptable to control electronic or electrochemical circuits. Two possible control systems are illustrated in figures 13 and 14.

The first system uses an electrolysis cell to supply hydrogen. (Solid polymer electrolyte membranes were particularly useful.) This hydrogen is either carried to the furnace in a water-saturated carrier gas (nitrogen, argon, etc.) to produce hydrogen-oxygen mixtures, or with carbon dioxide or carbon monoxide for carbon-oxygen-hydrogen (C-O-H) gas mixtures. For C-O-H gas, oxidizing conditions are most easily obtained by using carbon dioxide as the carbonaceous gas; reducing conditions are most easily obtained by using carbon monoxide. The output of the cell is used by means of feedback circuits to control the current to the electrolysis cell and consequently the rate of evolution of hydrogen (fig. 13).

For carbon-oxygen gas, the easiest way to control the gas is by changing the flow-controlling needle valves. The feedback circuitry is used to drive a reversible variable-speed motor that turns the needle valves. Figure 14 illustrates the gear-motor-feedback setup. The two needle valves are simultaneously turned in opposite directions.

These systems may be used in two ways. First, the oxygen fugacity may be fixed by using the null output of the meter and the feedback circuitry to maintain a preset emf automatically. Second, the furnace may be programed to execute a sequence of oxygen fugacity/time states by comparing the cell output (from the meter) with a time-varying emf signal (from multivoltage sources like those used to program temperature). The actual redox state of the system and the rate at which it can be varied are a complex function of system configuration, composition, and temperature.

Consequently, there is no a priori way to determine exactly how the system will behave. A control for feedback and rate of change should be provided in the circuit; they must be adjusted by the investigator for optimum control of his system.

Finally, the user is cautioned that hydrogen-containing mixtures form water during reaction in the furnace, which condenses after exiting the hot zone. Care must be taken that this water does not clog exhaust lines or thermally shock the electrode or muffle tube.

Sample Holder and Quenching System

The sample holder, fitting, and end plate design are shown in figure 15. Two types of holding devices are used: a metal spiral for solid samples and a wire loop for molten samples (ref. 12). Samples are either pelletized powders or chips of material and are either laid in the spiral basket or tacked to the metal loop by partly melting them in a strip heater. Alternately, the sample may be attached to the loop by partly melting it with an oxyacetylene minitorch.

Quenching is accomplished either by withdrawing the charge from the top of the furnace or electrically melting the thin (0.0102- to 0.0203-centimeter (0.004 to 0.008 inch) diameter) wire used to connect the sample to the heavy gage (0.076-centimeter (0.030 inch) diameter) support wires. For electrical quench, a port is provided on the base of the furnace (fig. 16), and this port must be carefully aligned with the sample holder. Because the gas flow is directed from top to bottom, the plug sealing the port may be removed without greatly affecting the redox conditions at the sample; the sample may be dropped through the port and quenched externally in water, liquid nitrogen, or any other appropriate quench medium. The plug is designed as a cup and the sample may be quenched in the furnace atmosphere by merely dropping it into this cup. Alternatives include placing a quench fluid in the cup or externally cooling the cup to facilitate the quench.

CALIBRATION

Millivoltage Sources

Millivoltage sources should be calibrated against a good standard; a potentiometer makes an almost ideal calibration device. The cell output fluctuations even in the best general-purpose system will limit measurements to ± 1 millivolt so that calibrations beyond this level are useless.

Temperature Calibration

In the JSC studies, the thermocouple inside the electrolyte cell is used to measure all temperatures, and this thermocouple should measure the same temperature as that which the sample experiences. This is accomplished by two sets of calibrations. First, the temperature distribution near the sample location is mapped

using the furnace in the actual run configuration and with the gas flow and sample holder in place but with the sample replaced by a thermocouple. This calibration gives the actual hot zone configuration and indicates the size of sample that can be run. This should be done at temperatures encompassing the temperature range over which the furnace will be used. Temperature calibration is required only once and needs to be repeated only if the furnace is rebuilt.

Finally, an absolute calibration is accomplished, again in the actual run configuration, by using convenient thermometric calibration points (sodium chloride, 1973.55 K (800.4° C); gold, 1337.55 K (1064.4° C); lithium metasilicate, 1475 K (1202° C); diopside, 1668 K (1395° C); anorthite, 1828 K (1555° C)).

Graphical monitoring of temperature with automatic compensation for ambient temperature is very convenient. Temperatures should occasionally be checked with a potentiometer.

Electrode Calibration

The electrode itself should be checked for correct emf response. Most errors in calibration are due to incorrect electronic hookup or incorrect placement of the sample relative to the electrode. The three most convenient calibrations are against air, the nickel-nickel oxide (NNO) buffer, and the iron-wüstite (IW) buffer. The electromotive forces of the cell in millivolts with pure oxygen gas as a reference are given by the following equations:

$$\text{Air: } E = -0.0337T$$

$$\text{NNO: } E = -1267 + 0.511T$$

$$\text{IW: } E = -1350 + 0.326T$$

where T is in kelvin. Note that the electromotive forces are always negative within the operational temperature range. The polarity of the electronic setup can be rapidly checked. The best procedure is to reverse the metal/metal-oxide buffer reactions using metal foils as a starting material and duplicating actual run configurations as far as possible. The use of foils is convenient because the calibration is a tarnish technique and the tarnish forms or dissipates in approximately 15 minutes.

RUN PROCEDURES

Assuming that one is starting from a completely down condition, the reference flow to the electrode is begun. The temperature of the furnace is then increased slowly to approximately 1473 K (1200° C). The emf from the electrode is monitored during this procedure; with the furnace open to air, the electromotive forces are

near those of the air/oxygen couple. In a dynamic system, these electromotive forces are rarely attained precisely, but an approximately correct response indicates that the electrode and electronics are functioning correctly. At approximately 1473 K (1200° C), the furnace is sealed and carbon dioxide is flowed through the furnace for a few hours to degas the system. Finally, pure carbon monoxide is run through the furnace, and the emf output of the electrolyte cell should exceed 1000 millivolts at 1473 K (1200° C). If it does not, either an air leak exists in the system and all the seals must be checked or the electrical contacts within the cell are loose and must be tightened.

After this "baking out," the gas flow is adjusted to run conditions. The exhaust valve from the furnace is set full open, and the mixing needle valves are each set half open. The gas feed pressures are set between 6.9 and 27.6 kN/m² (1 and 4 psig) on the low-pressure regulators. The needle valves controlling the input gases are adjusted until the desired total flow is obtained: 0.0085 to 0.01416 stdm³/hr (0.3 to 0.5 stdft³/hr) is sufficient. The exhaust valve is closed until the flow is just affected. (This procedure slightly pressurizes the furnace, minimizing leakage of air into the furnace.) To change the oxygen fugacity, the mixing ratio is adjusted by turning both needle valves, always opening one while simultaneously closing the other. The calibration procedures for the thermocouple and cell are then performed; these are generally not repeated until the system is rebuilt.

A sample is inserted into the furnace by placing the sample holder in the sample port. When this port is opened, a slight burn-off may appear at the top of the furnace. This is not serious, but the sample should be inserted immediately to prevent the burn-off from flashing back into the furnace. When initially inserted, the sample is held near the top of the muffle. It is gradually lowered (in steps) into the hot zone over a 10- to 15-minute period to permit the sample to degas and gradually adjust to the high-temperature environment. The temperature and f_{O_2} may change slightly after the sample is inserted because of degassing of the sample and sample holder and their thermal mass. Conditions should return to the original settings within 5 or 10 minutes; if not, only the slightest adjustments should be necessary. If the quench port is opened, the orientation of the sample and the electrode can be examined with a mirror. Because of the gas-flow pattern, the redox conditions near the sample are not affected by opening this port. The quench is accomplished by electrically burning the fine platinum wire and dropping the sample through the quench port.

Further runs are conducted by insertion and removal of samples and adjustment of mixing ratio and temperature. Fluctuations of ± 1 to ± 3 millivolts over day-long periods are normal.

When a programmed temperature change experiment is to be performed, the following procedure is used. The furnace is stabilized at the lowest temperature desired, the programmer is interfaced with the system, and the furnace is brought to the highest temperature by subtracting millivoltage from the thermocouple with the programmer. When this condition is stabilized, the sample is inserted and the drop accomplished by progressively changing the millivoltage with the programmer.

A temperature rise experiment is performed by reversing this procedure. This technique has the advantage of absolutely fixing the beginning and end points of experiments and ensuring that the system is controlled by the furnace controller at the end of an experiment.

PRECAUTIONS

The ceramics used to make the electrodes are very sensitive to thermal shock at temperatures above approximately 773 K (500° C). Once the electrode is in place and the heating process is begun, it is best to restrict the movement of the electrode to an absolute minimum. This is accomplished by mounting the electrode so that the sensing head is in the center of the hot zone of the furnace. Any subsequent alignment is accomplished by adjusting the sample position only. To prevent thermal shocking, the reference gas-flow rate is kept as low as possible.

Finally, during the cooling of the furnace, the furnace must either be opened to the air or the gas flow must be continued during the cooling; otherwise, a substantial vacuum can be created.

COMMON PROBLEMS

Erratic emf Output

All shielding, grounds, and electronic connections must be checked. Leads should be firmly connected to the electrode, and it should be ensured that there is no short circuit to the temperature measurement system.

Incorrect emf Output

All ground loops must be eliminated; all metal surfaces must be grounded. If these sources of error have been eliminated, the only other sources of incorrect electromotive forces are miscalibration and misalignment of sample and electrode.

Drift

At highly reducing conditions, graphite or water (or both) form in the system. These clog the output flowmeters and lines affecting the gas flow. The lines should be checked for condensation and should be cleaned. The needle valves used for mixing can wear out and may slip. Drift caused by changes in gas composition will be noted when bottles begin to be depleted, particularly if gas mixtures are used (hydrogen in nitrogen or carbon monoxide in nitrogen). Drift may also occur if the metallic contact to the electrode is not firm.

Overshoot

In adjusting the mixing ratio, changes of the gas mixture take a finite time to be effective in the furnace. This time varies with the flow rates used and with the construction of the gas mixer. It is best to adjust the mixing ratio slowly and in small steps to prevent overadjustments. The change in the f_{O_2} and that in the

mixing ratio is not linear; depending on the particular conditions of the experiments, varying amounts of adjustment are needed to effect the same change.

Old Age

After a cell has been used for several months, the metallic contacts grow through the ceramic to produce partial electrical short circuits. Erratic emf outputs, incorrect emf response, and drift can occur unpredictably. This problem is seen only in cells that have been in continuous use for several months, and the solution is to replace the cell with a new one.

MAINTENANCE

Although the lifetime of the system is theoretically very long, in practice the system functions only for 8 to 12 months before some component breaks down. When this occurs, one must perform a complete maintenance check of the system, which includes the following items:

1. Replace all wiring and contacts in the cell.
2. Check all O-ring seals and grease or replace, if needed.
3. Check plumbing and clean flowmeters and valves.
4. Check and clean water cooling system.
5. Recalibrate for temperature and oxygen fugacity.

By following this procedure, it is possible to reduce downtime significantly. All items used for maintenance are minor.

The furnace may, under some conditions of use, become saturated with water or graphite. This condition makes itself evident by drifting electromotive forces, sluggish response, and general instability of redox conditions. It can be remedied by opening the top and bottom ports of the furnace and allowing it to operate at about 1473 K (1200° C) for about 24 hours. This procedure dehydrates the furnace and "burns out" the graphite. It is necessary to do this every 4 to 6 weeks.

CONCLUDING REMARKS

This experimental system for measuring oxygen fugacities in gas-mixing systems should be useful to investigators engaged in research in which control of redox conditions is necessary. The system was developed in conjunction with a variety of studies performed at NASA Lyndon B. Johnson Space Center where the capability and utility of the system have been verified. Investigators at Lyndon B. Johnson Space Center have established and validated the procedures for operating, calibrating, and maintaining the system. These researchers believe that the system is the simplest and least expensive one available and that it should be useful in a variety of experimental applications.

Lyndon B. Johnson Space Center
National Aeronautics and Space Administration
Houston, Texas, October 29, 1975
383-35-00-00-72

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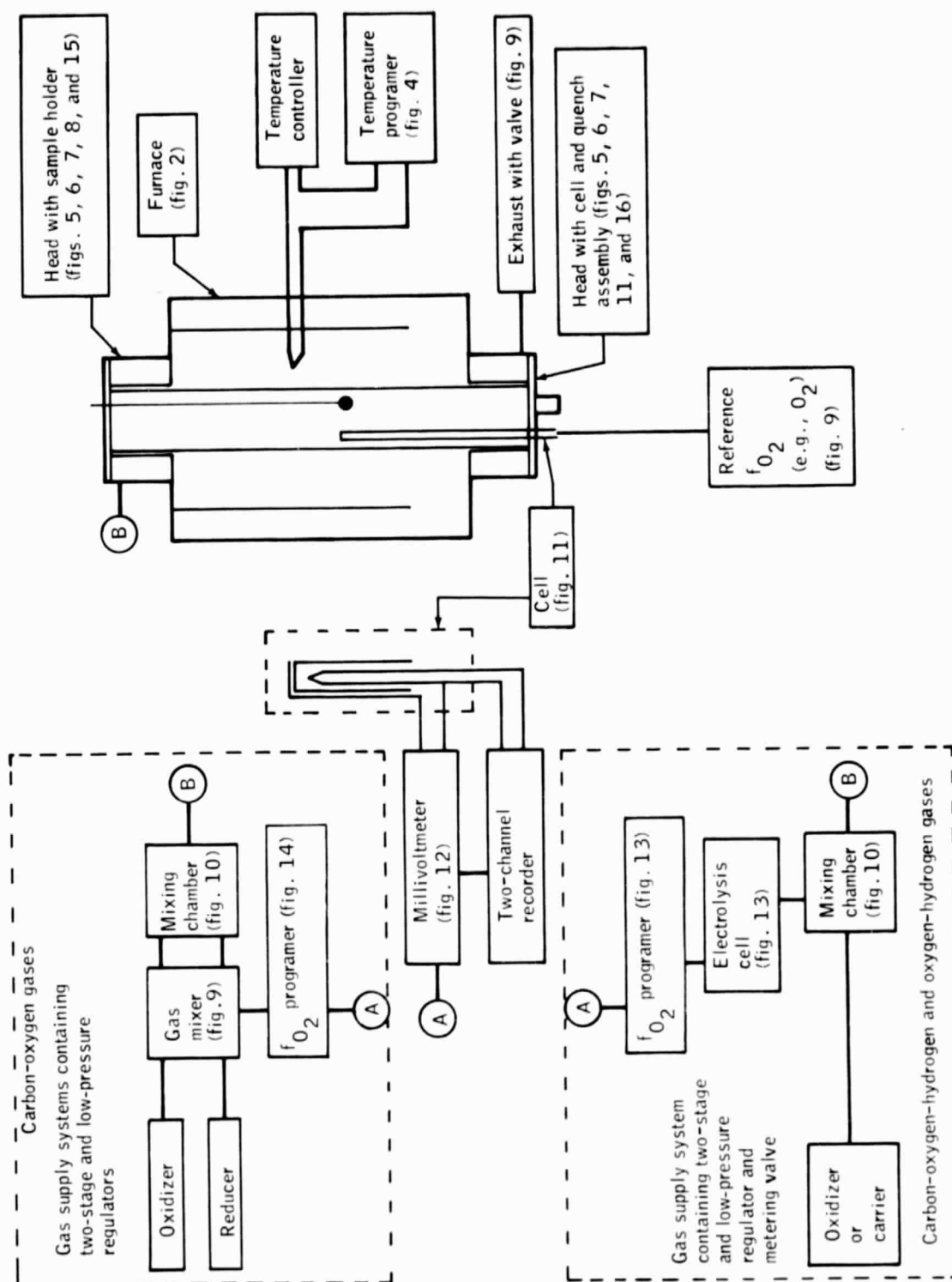


Figure 1.- Block diagram of JSC gas-mixing system. Components are shown in greater detail in the figures indicated in parentheses.

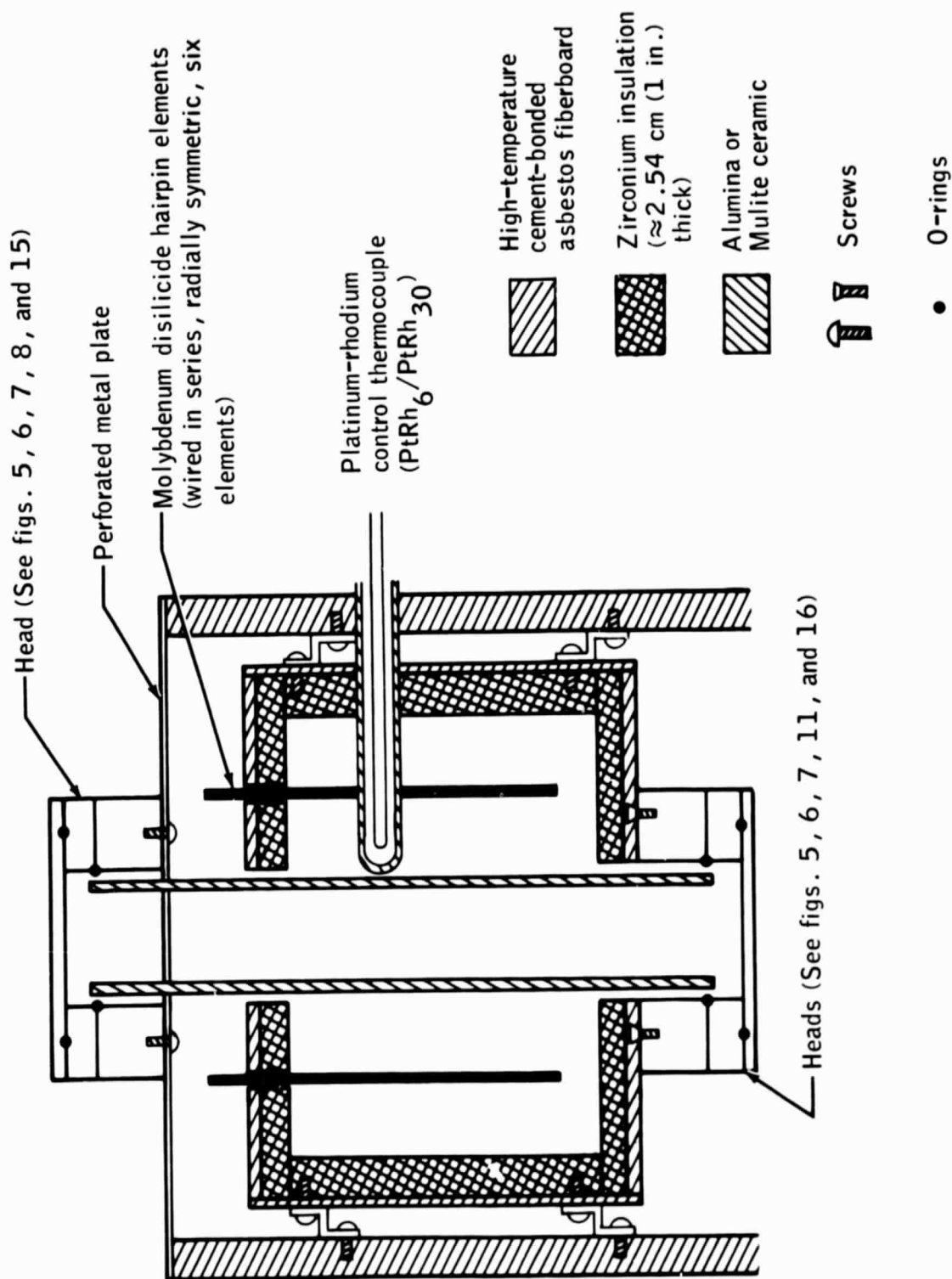


Figure 2.- Construction of high-temperature furnace (cross section; not to scale).

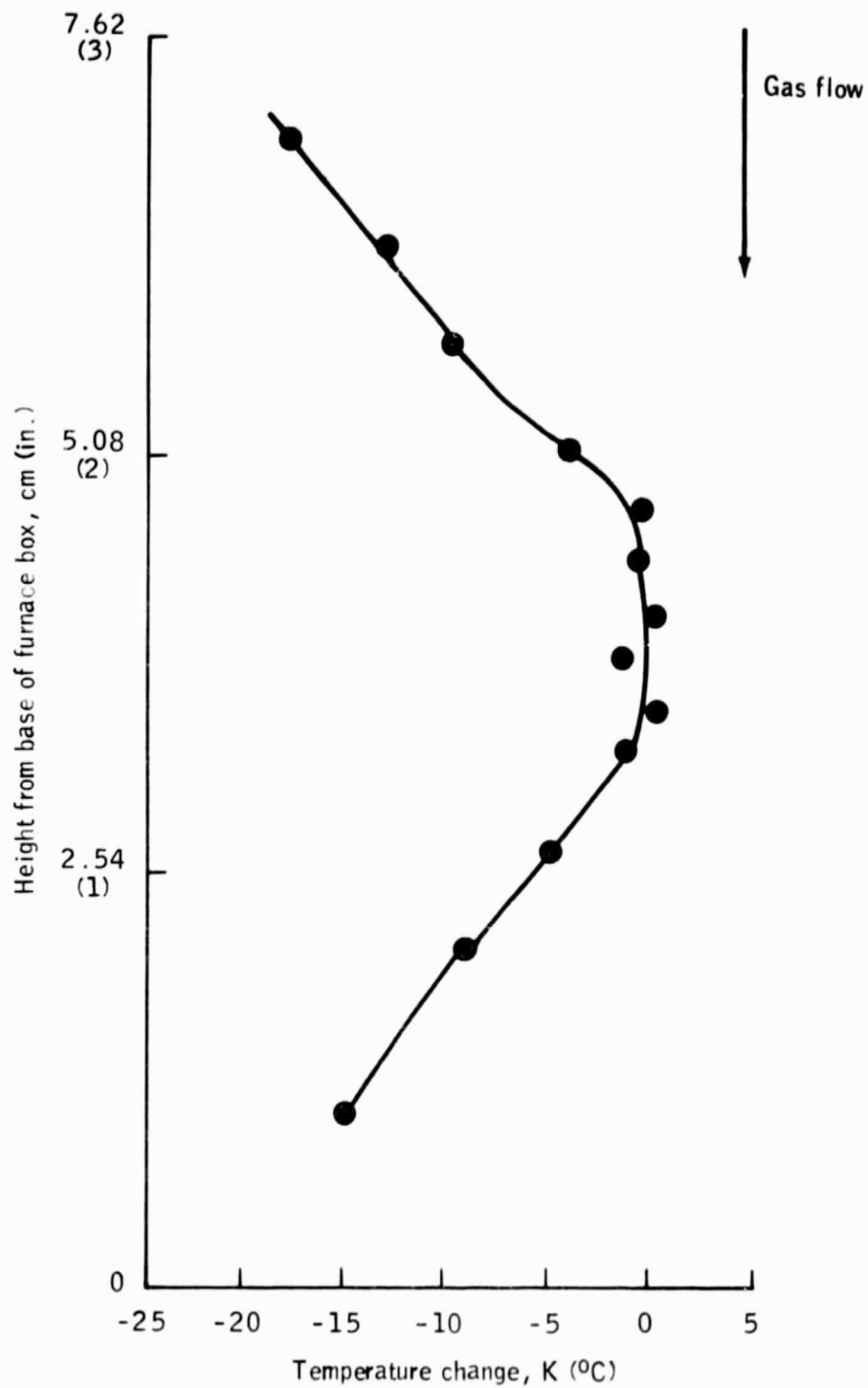
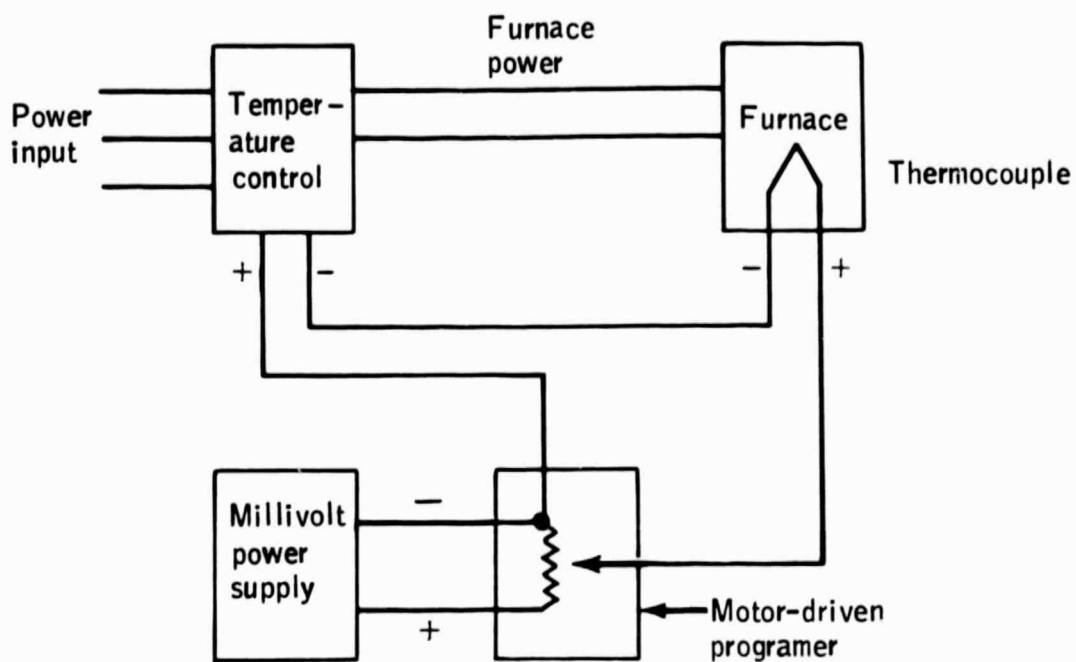
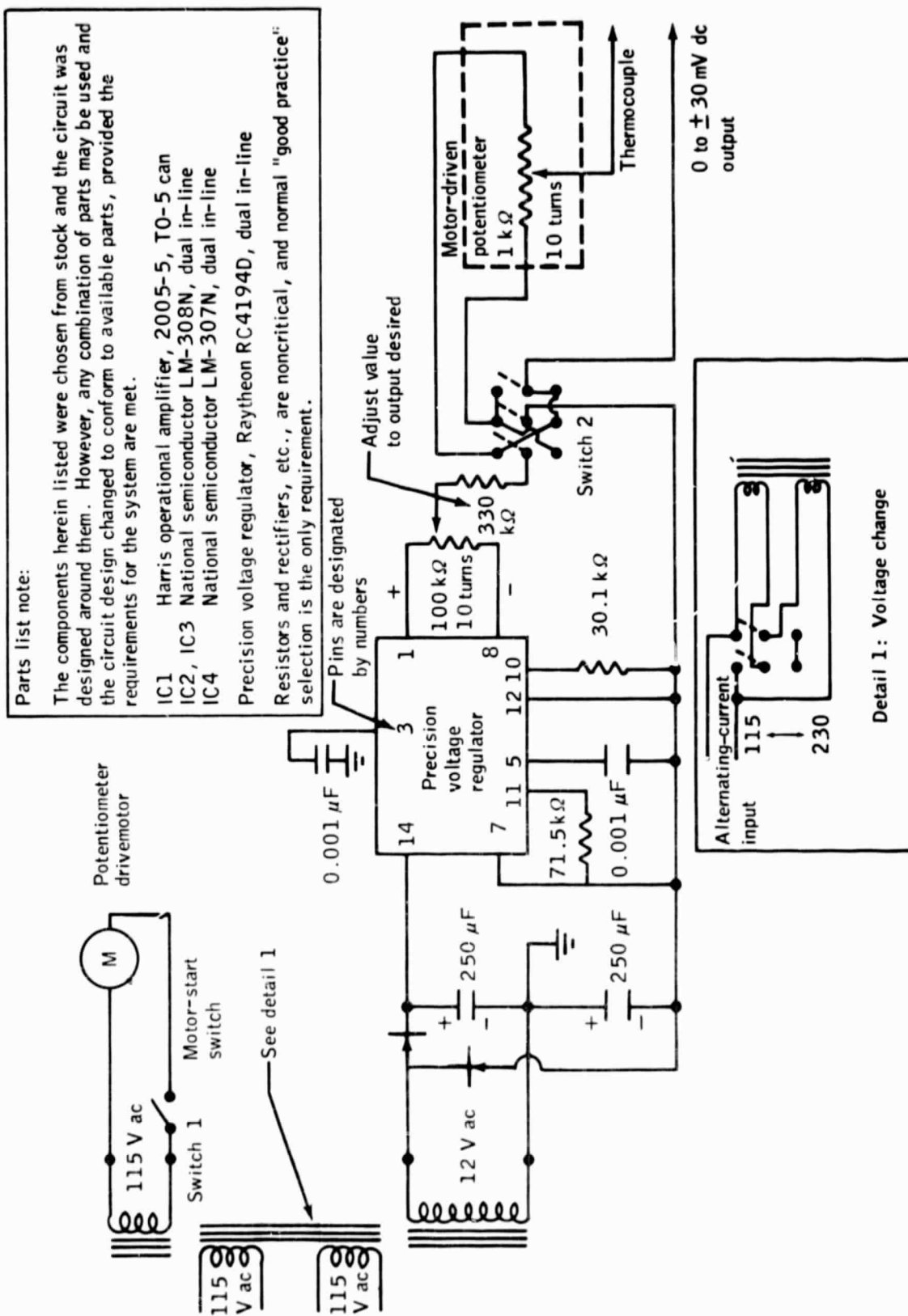


Figure 3.- Profile of hot zone. Average results for 1273, 1473, and 1673 K (1000°, 1200°, and 1400° C) hot-spot temperatures.



(a) Block diagram of wiring. Any low-voltage, well-regulated, direct-current power supply may be used.

Figure 4.- Temperature programmer.



(b) Electromechanical temperature programmer.

Figure 4.- Concluded.

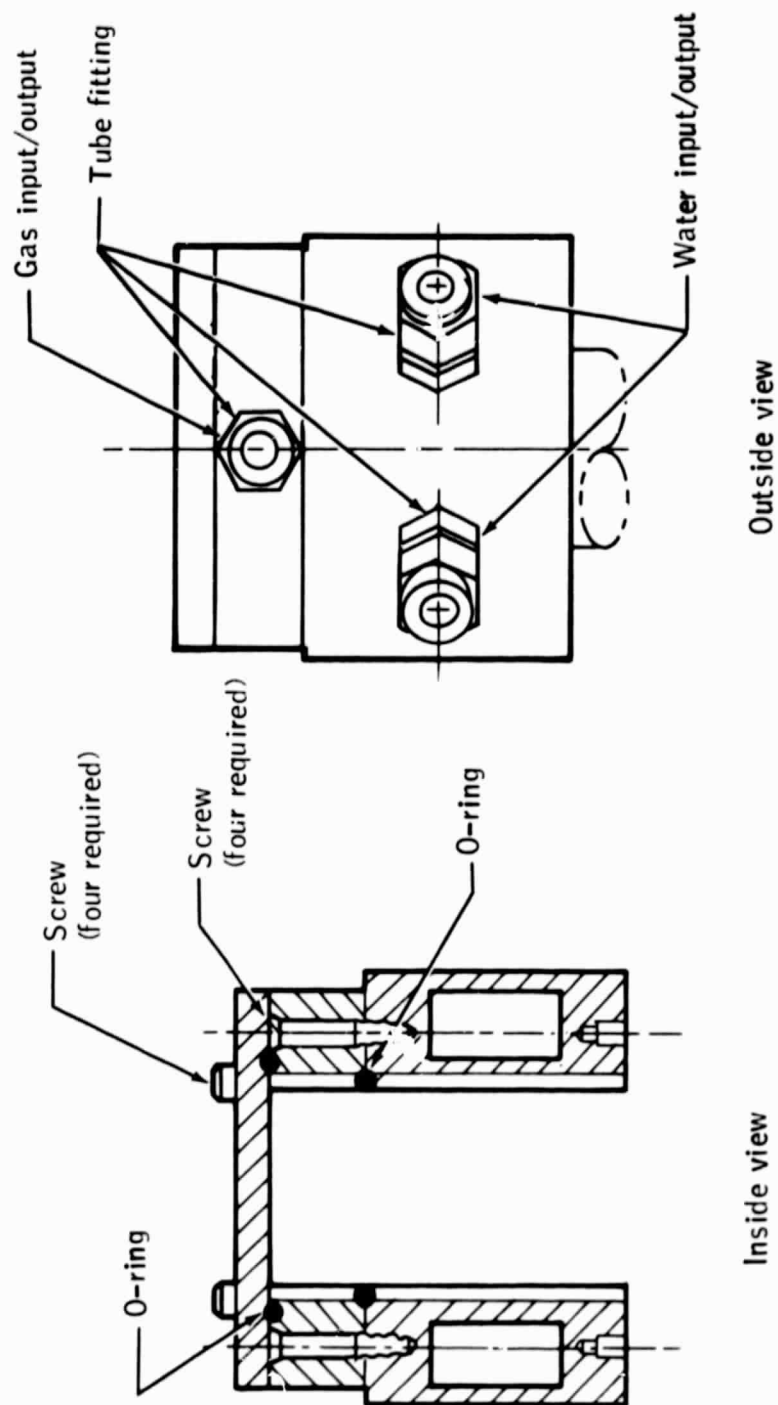


Figure 5.- Water-cooled furnace seals .

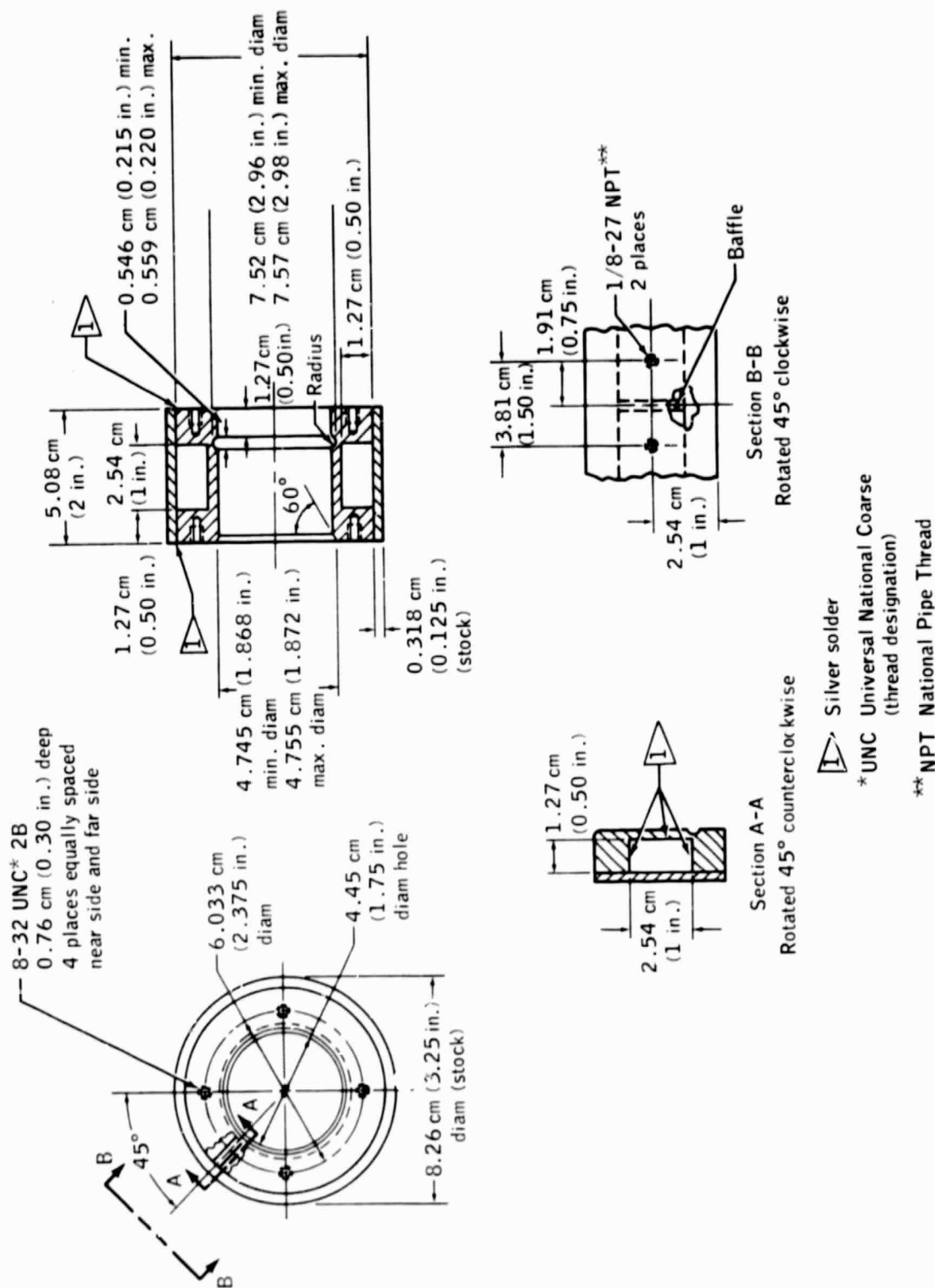
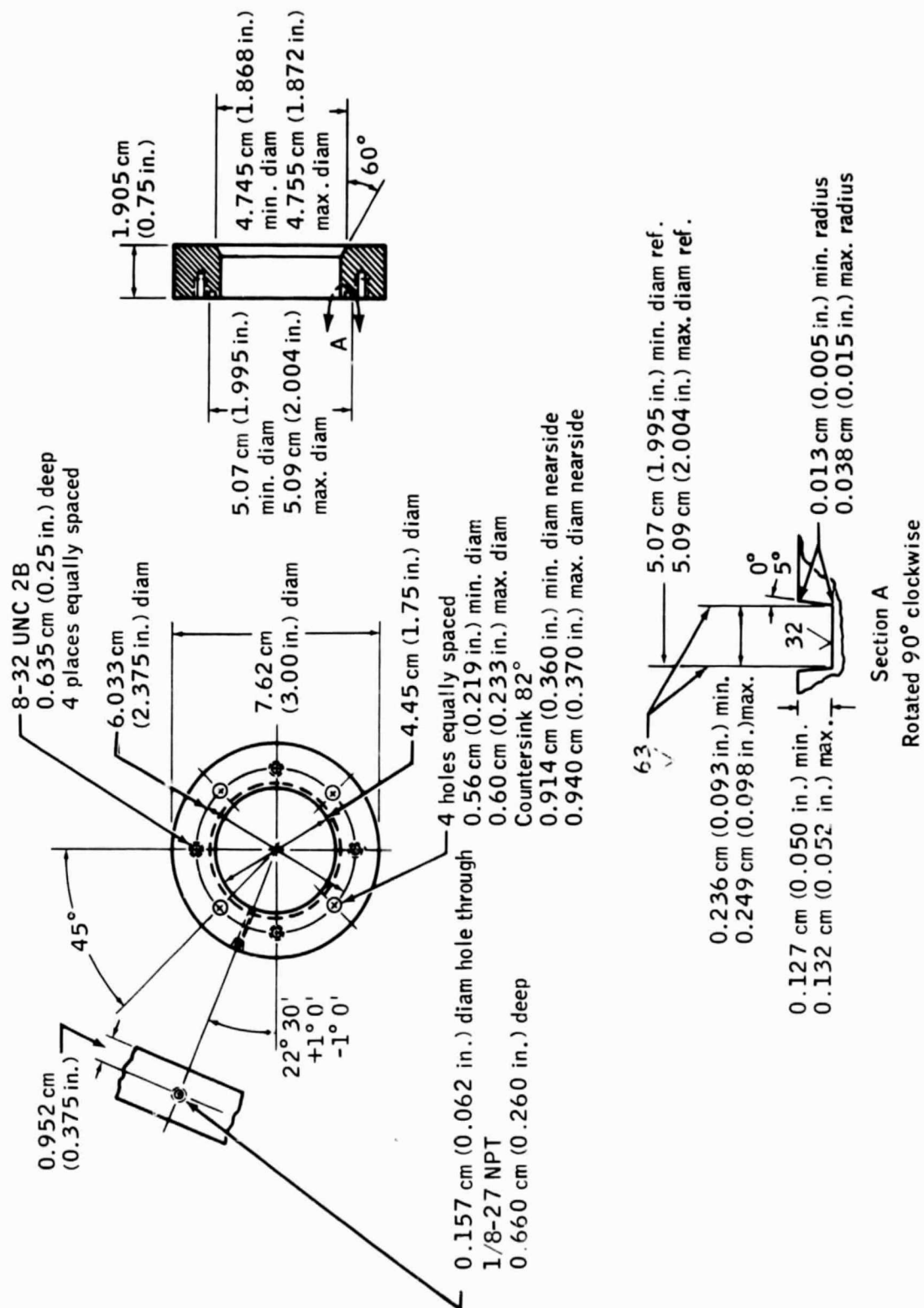
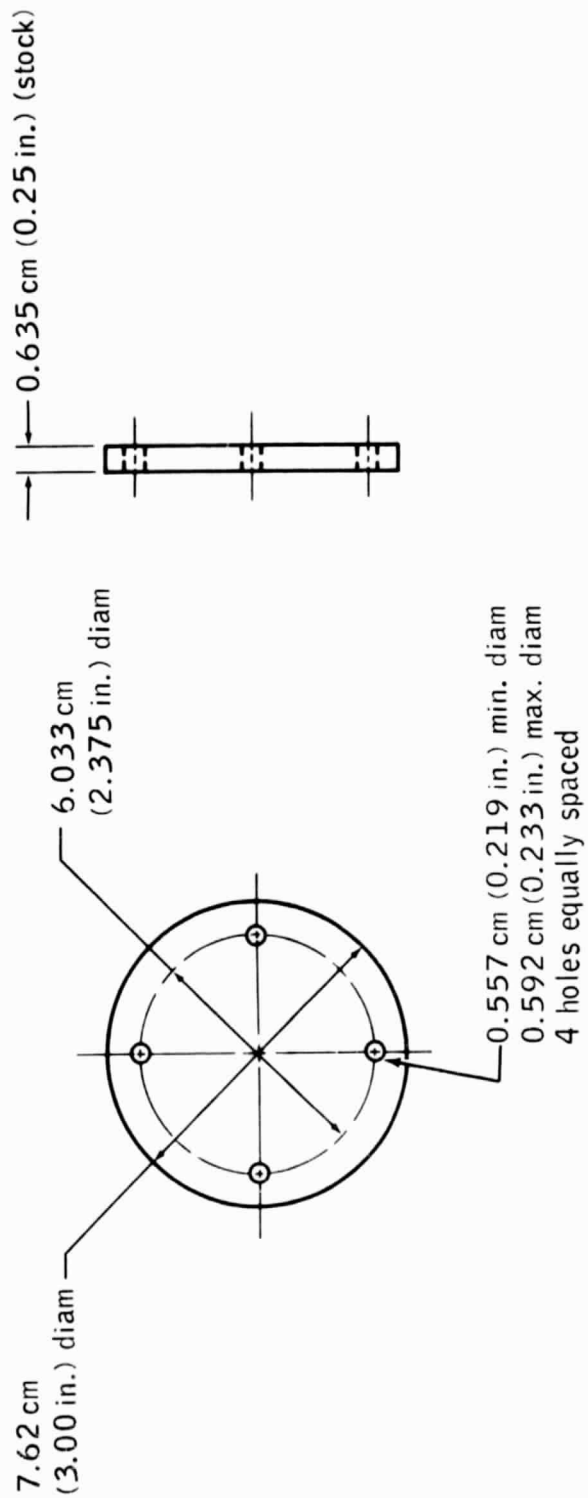


Figure 6. - Detail of water-cooling ring. To obtain uniform waterflow, a baffle is silver soldered between the input and output fittings inside the head (section B-B) before the water jacket sleeve is soldered in place.



(a) Sealing ring.

Figure 7.- Detail of gas seal.



(b) End plate.

Figure 7.- Concluded.

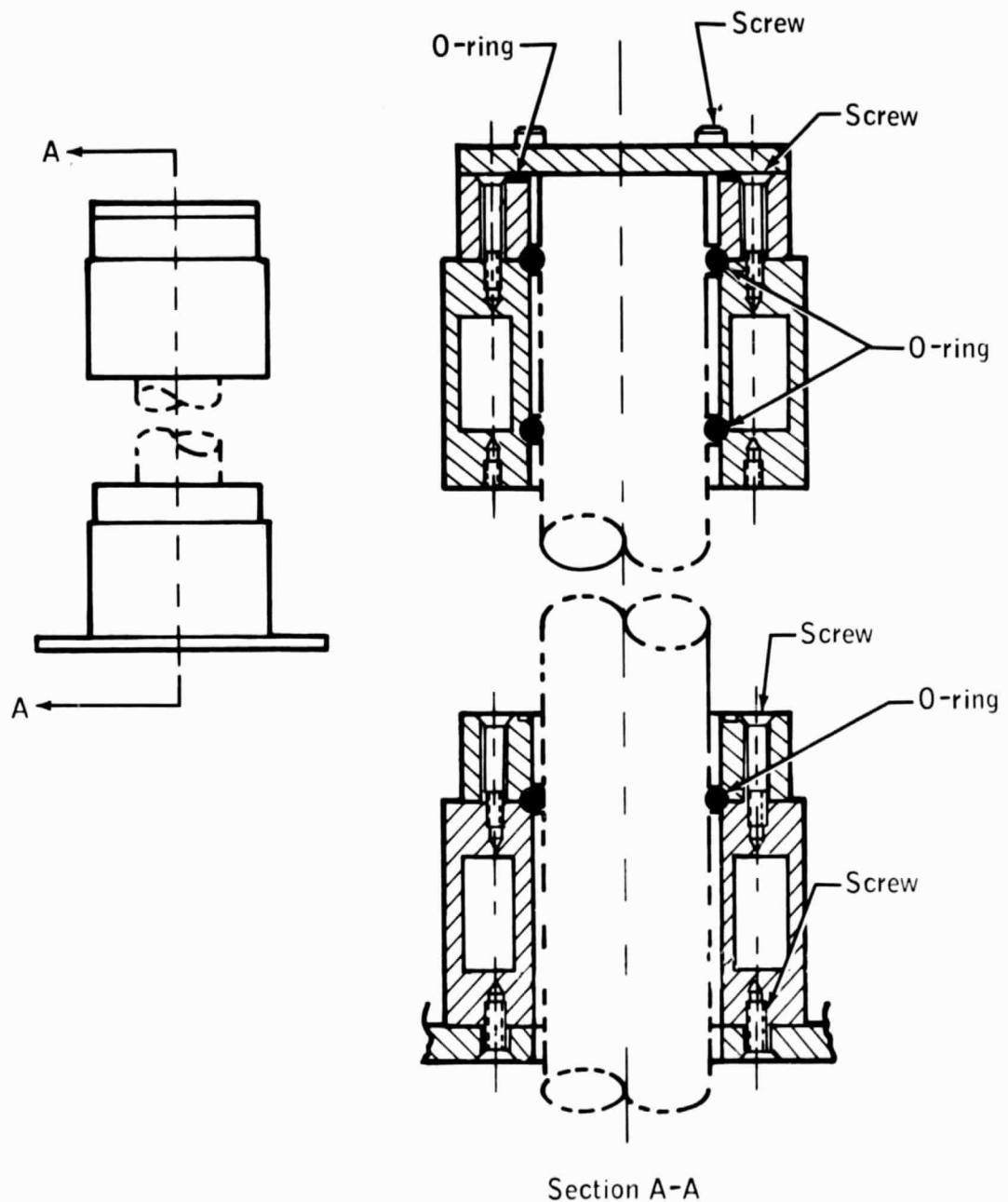


Figure 8.- Dual head arrangement for large-bore furnaces. Note that, for this arrangement, two O-rings are necessary at the top head to ensure alinement of the heads.

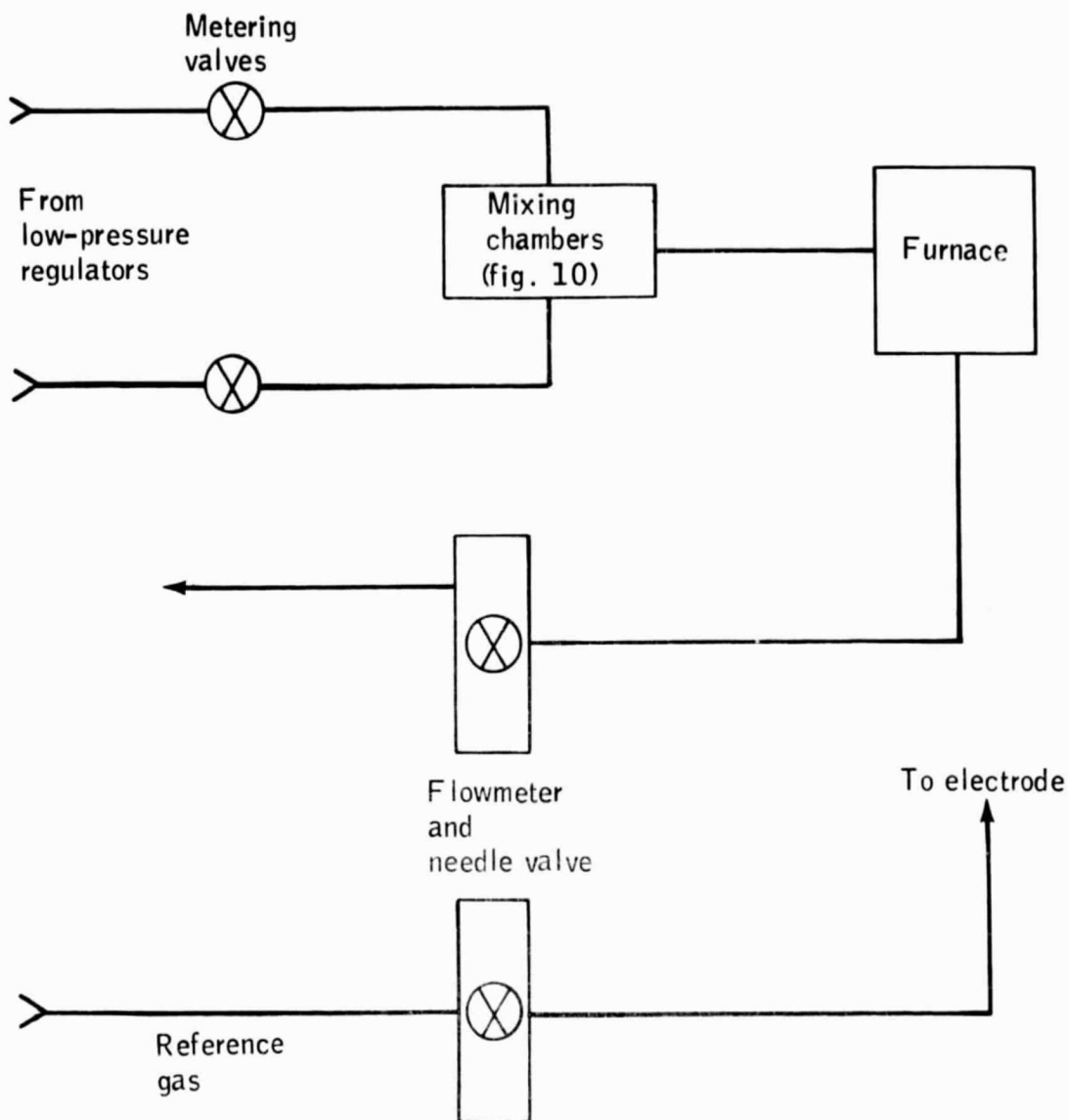


Figure 9.- Schematic of gas mixer. Flowmeter on furnace flow has 0 to 0.0283 stdm^3/hr (0 to 1 stdft^3/hr) range; flowmeter on reference gas, 0 to 0.0029 stdm^3/hr (0 to 0.1 stdft^3/hr). Metering valves are multiturn and should be of sufficient size to just meet total flow demand for the furnace (approximately 0.0170 stdm^3/hr (0.6 stdft^3/hr)).

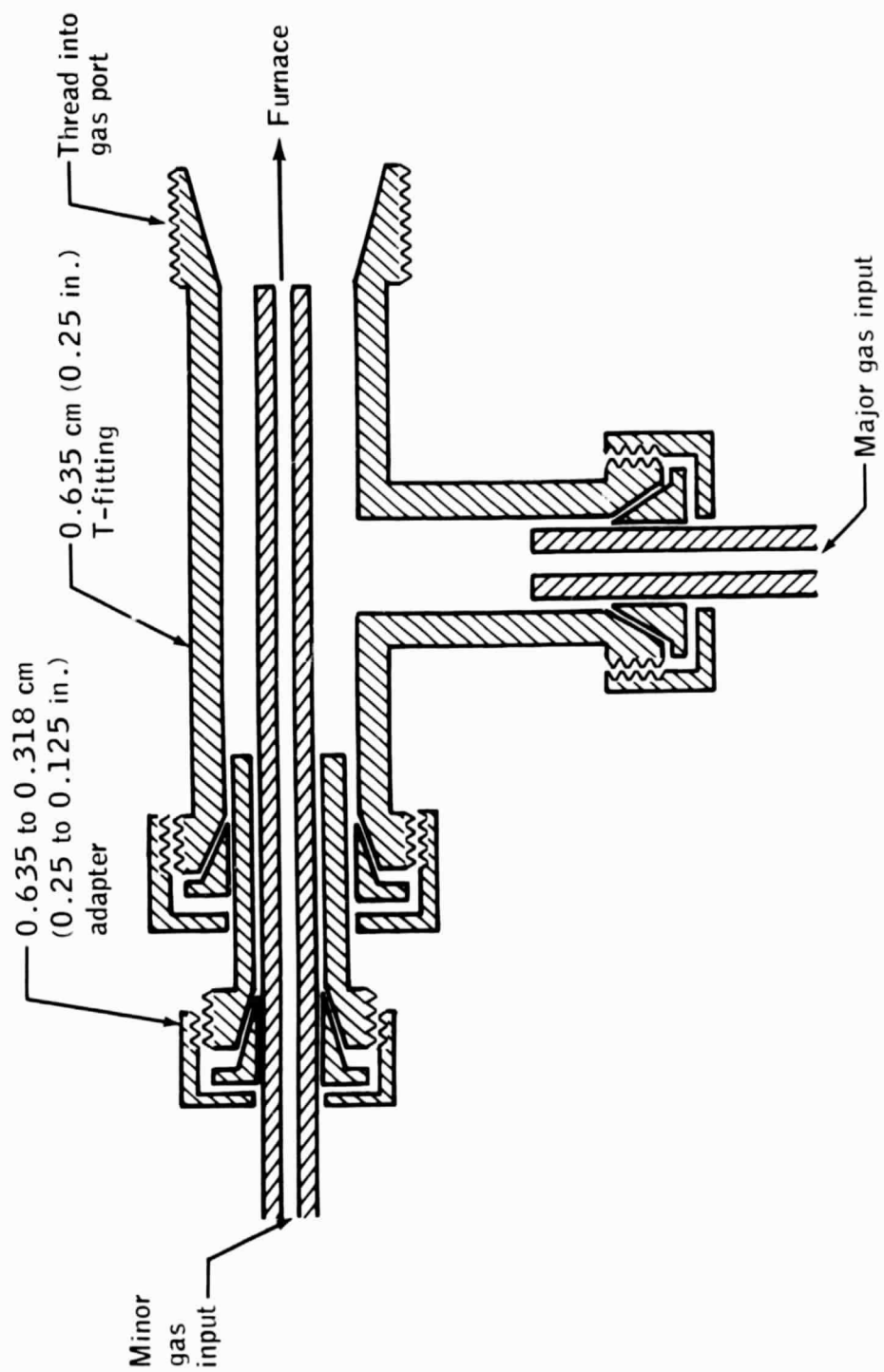


Figure 10.- Mixing chamber (not to scale).

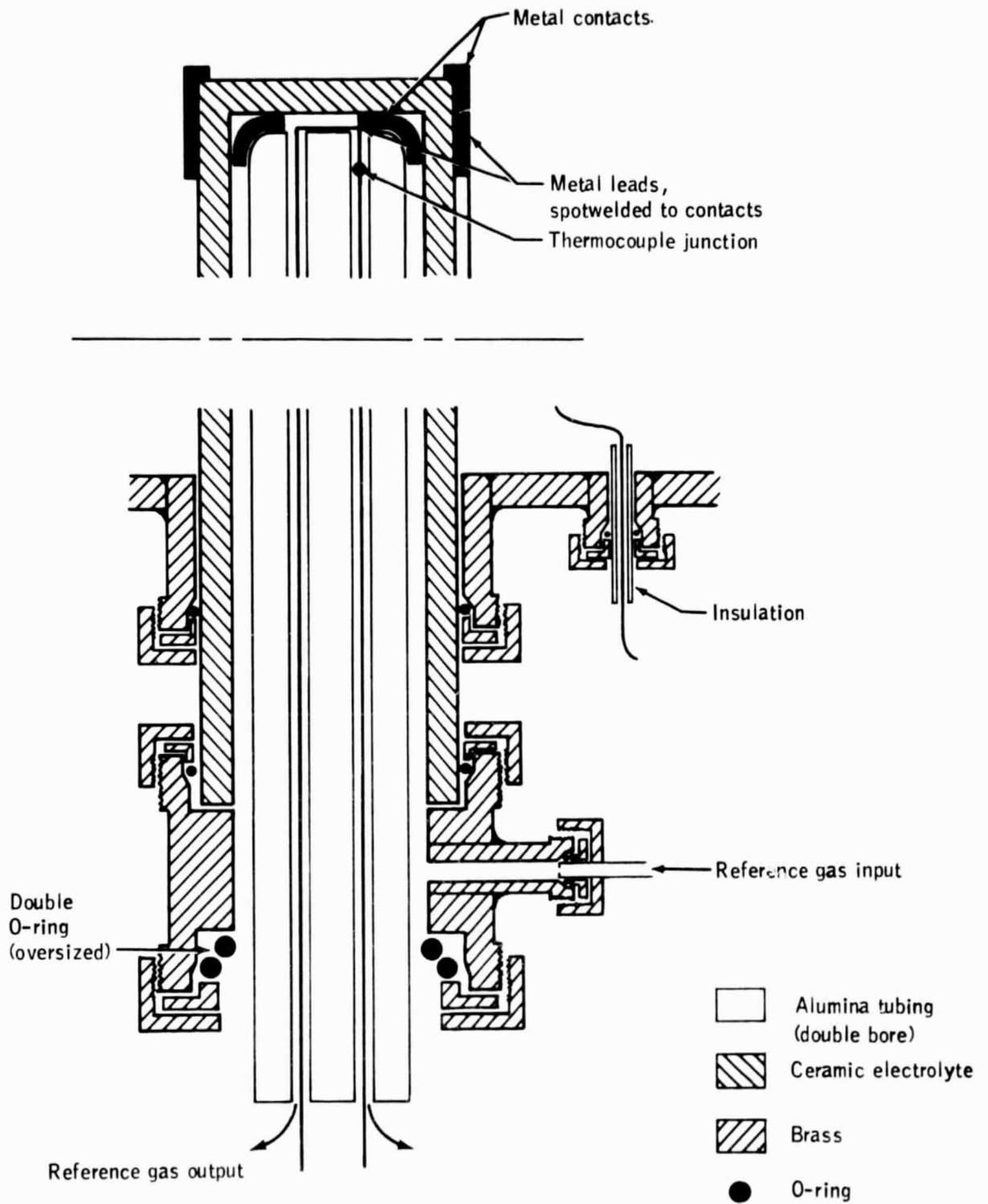
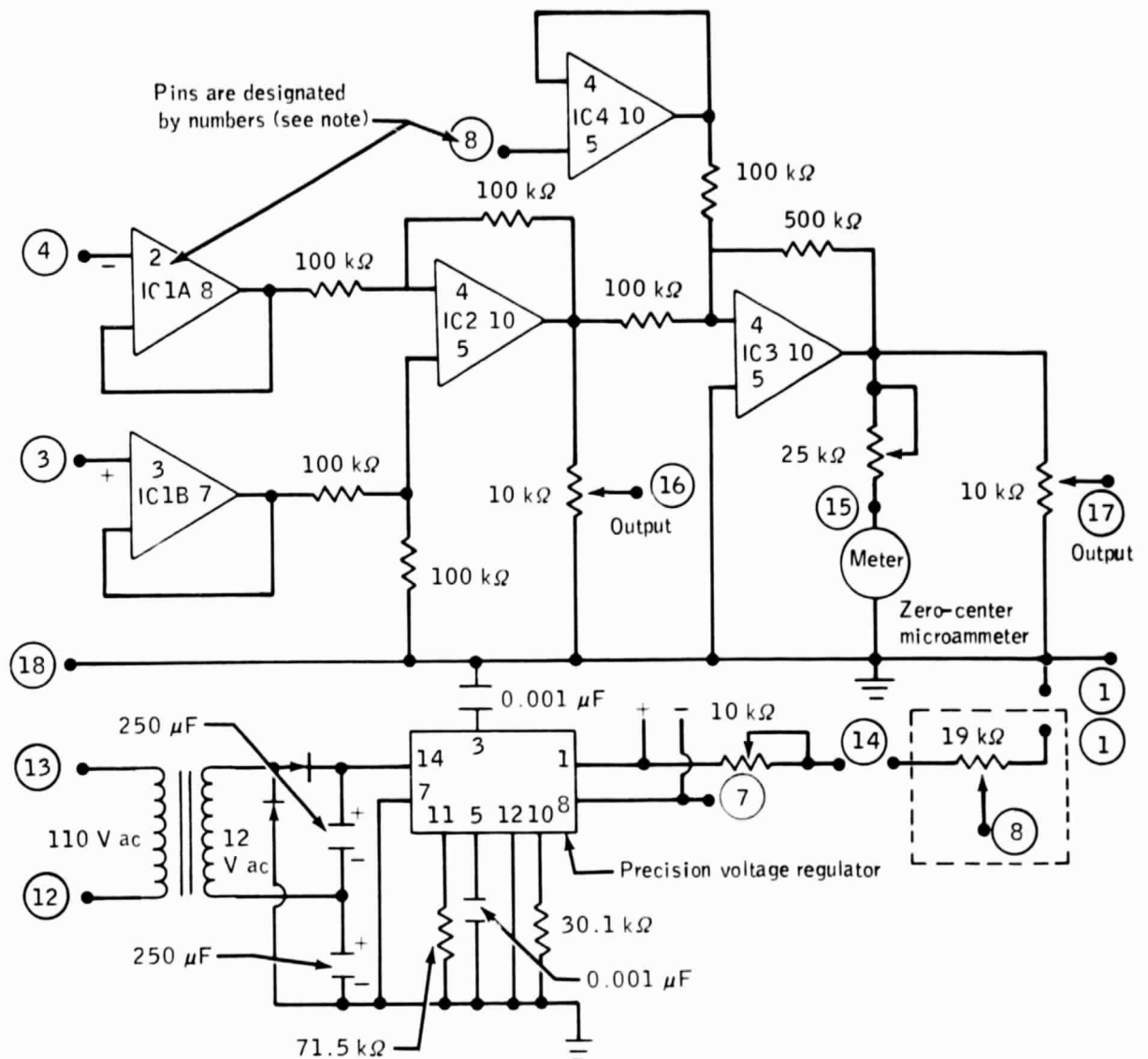


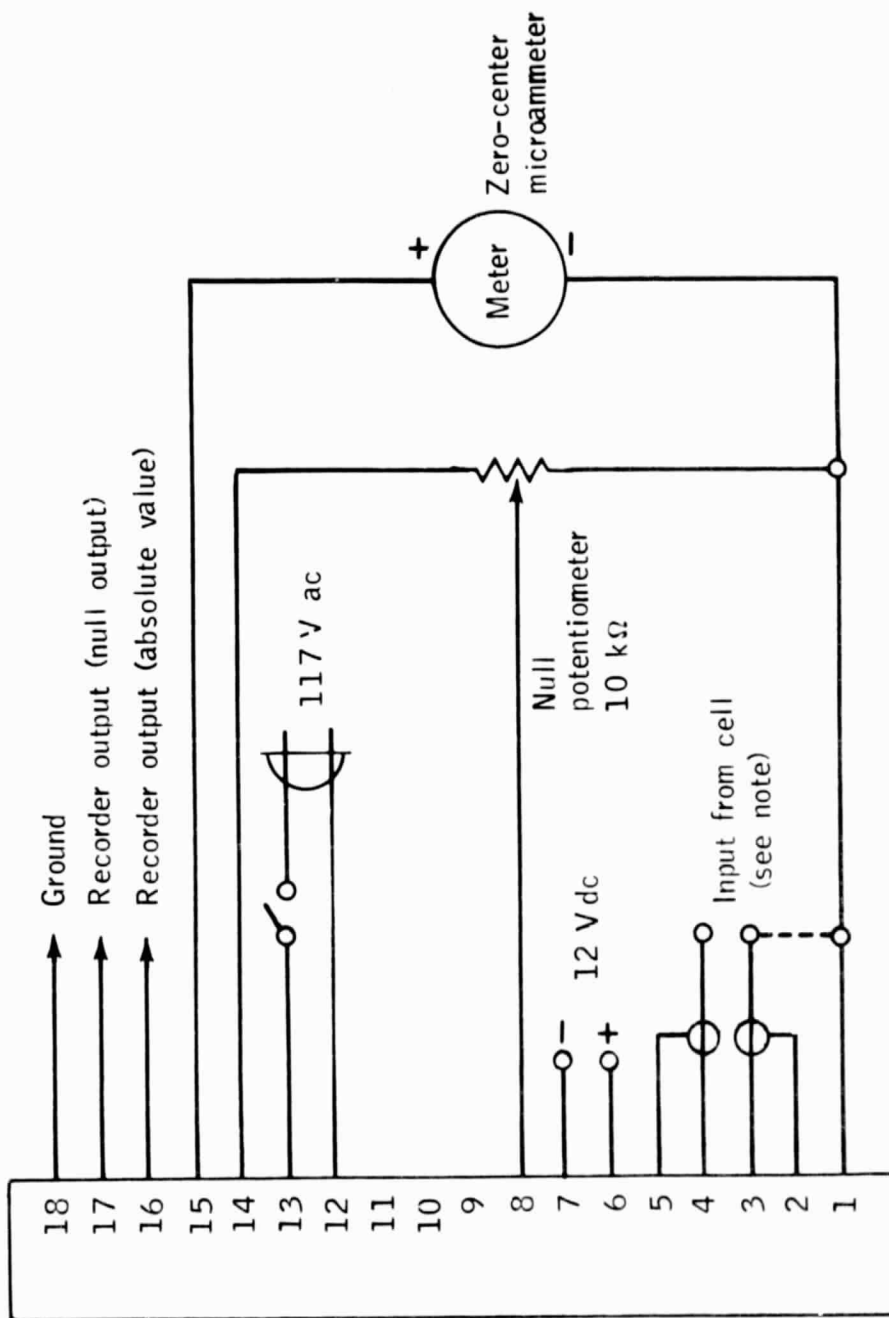
Figure 11.- Construction and mounting of solid ceramic electrolyte oxygen concentration cell (not to scale).



Note: For automated control, connect the output from the programmer (fig. 4) to pin 8. Set the output of the programmer for null at the f_{02} and temperature desired and then program the f_{02} change according to the same procedure as for temperature programming. This procedure provides a variable reference to IC3 causing a constant offset. This offset is used to drive an electrolysis cell or motor-driven valves. (See parts list note in figure 4(b).)

(a) Schematic.

Figure 12.- Differential millivoltmeter.



Note: Best results are obtained if pin 3 is grounded. This lead is shared with the thermocouple, and grounding prevents direct-current offsets from occurring.

(b) Wiring connections to printed circuit card.

Figure 12.- Concluded.

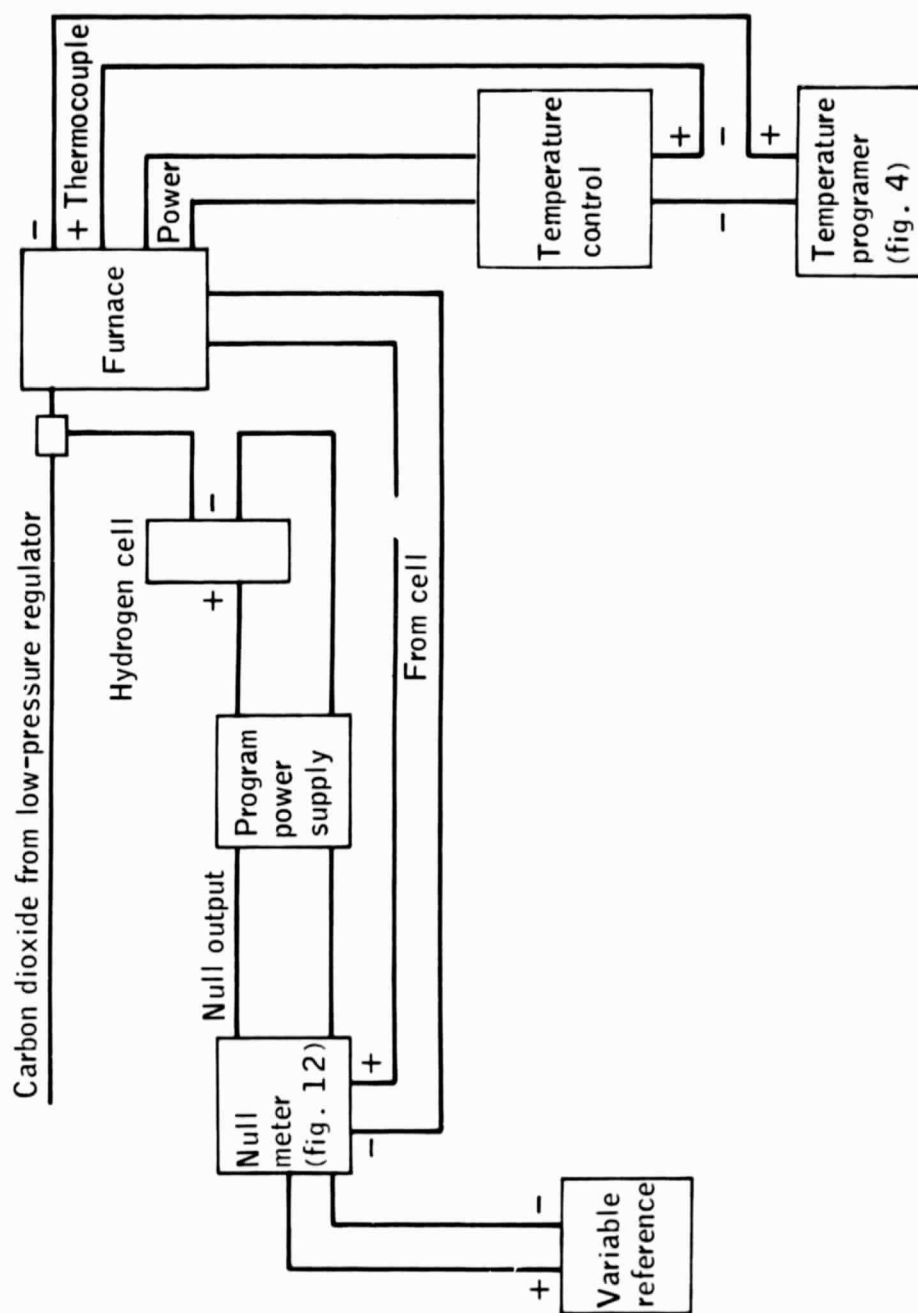


Figure 13.- Electrolysis cell oxygen fugacity programming system. Variable reference is obtained from a power supply like that shown in figure 4(b), but change 330-k Ω resistor to give maximum 1.5 V dc output. Also see note in figure 12(a).

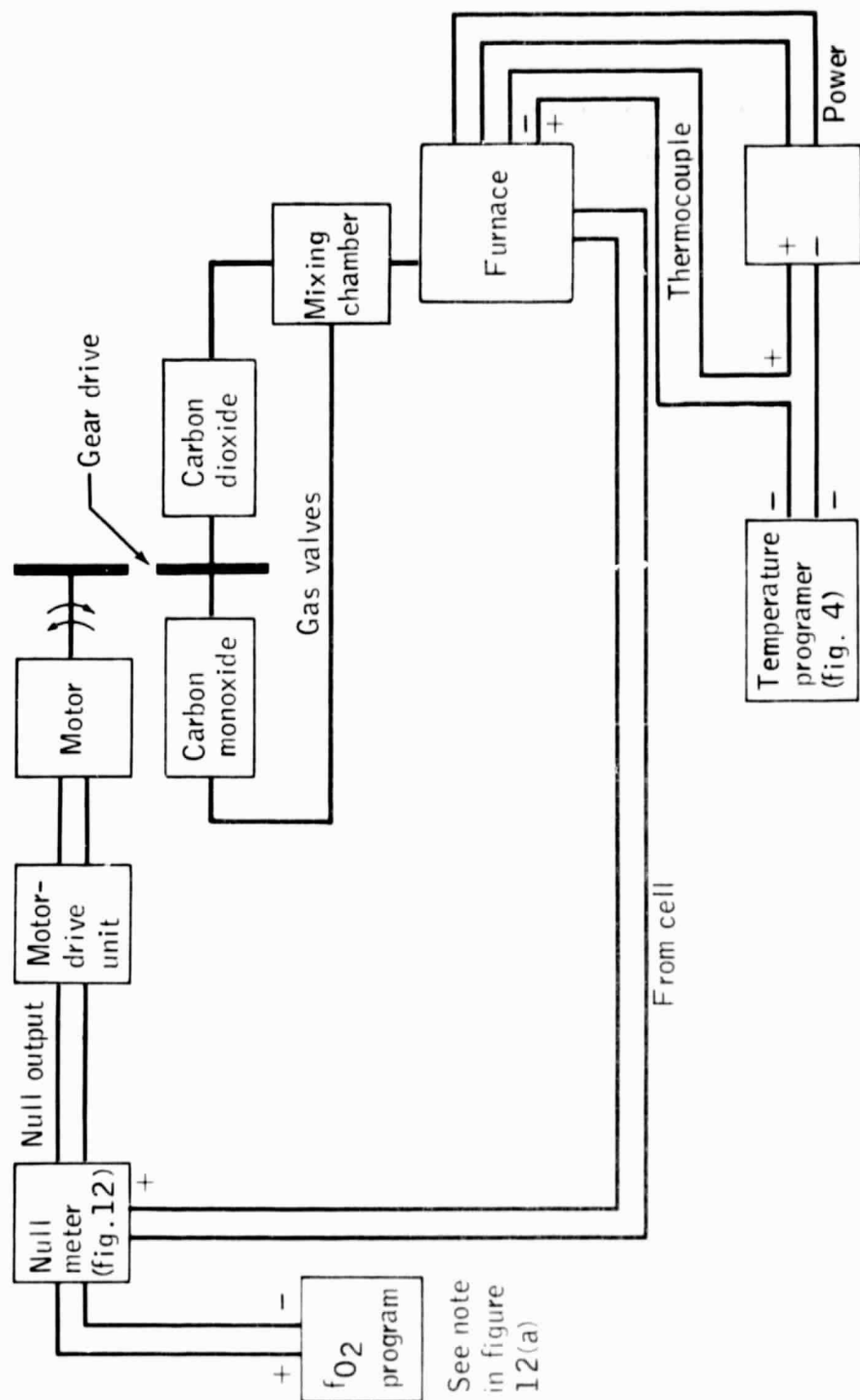


Figure 14.- Electromechanical oxygen fugacity programmer. (See figure 13 and note in figure 12(a)).

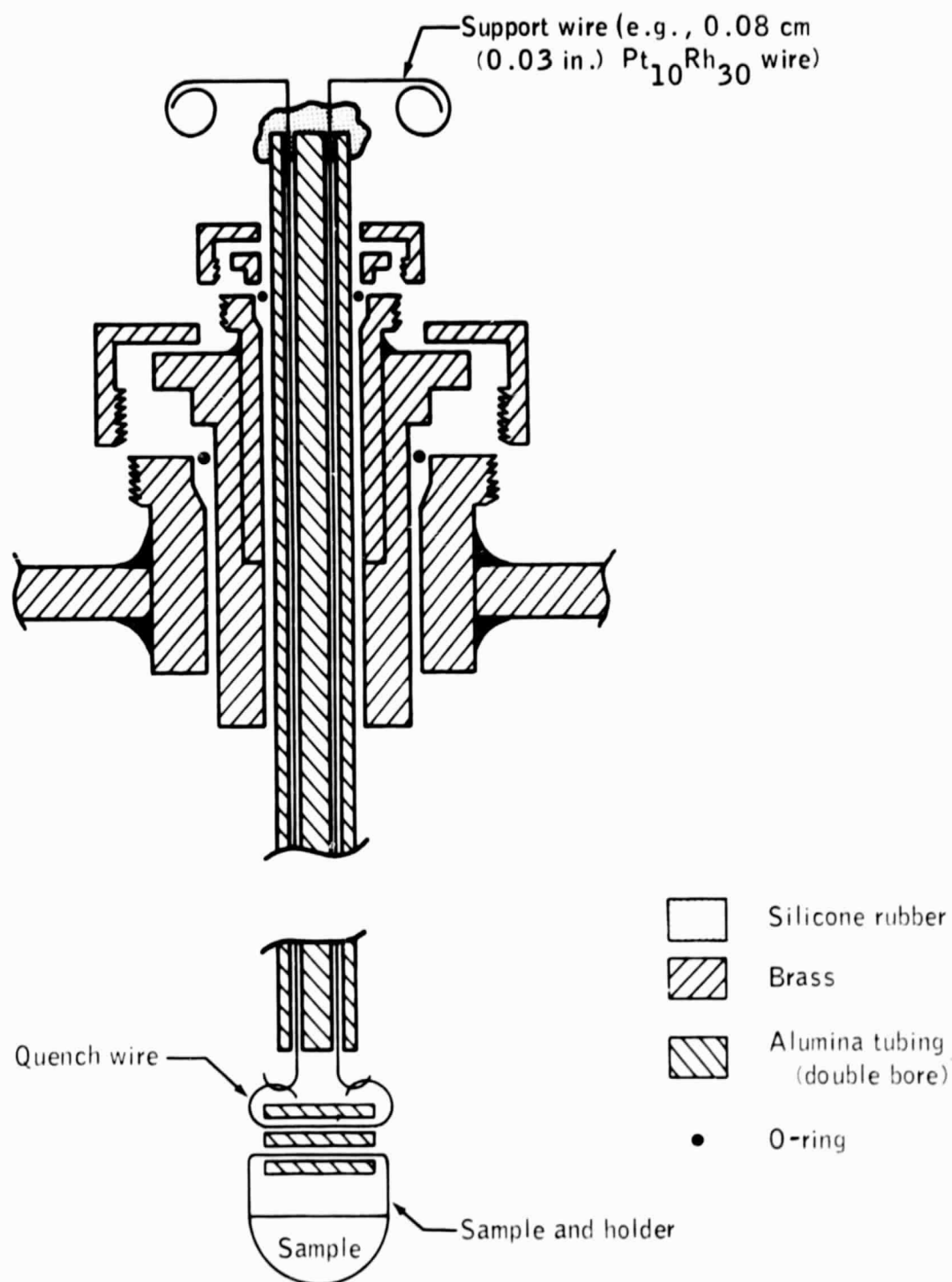
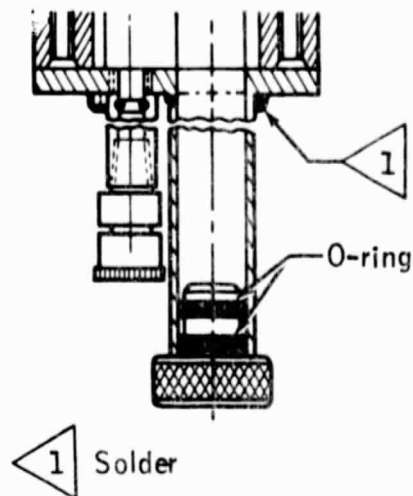
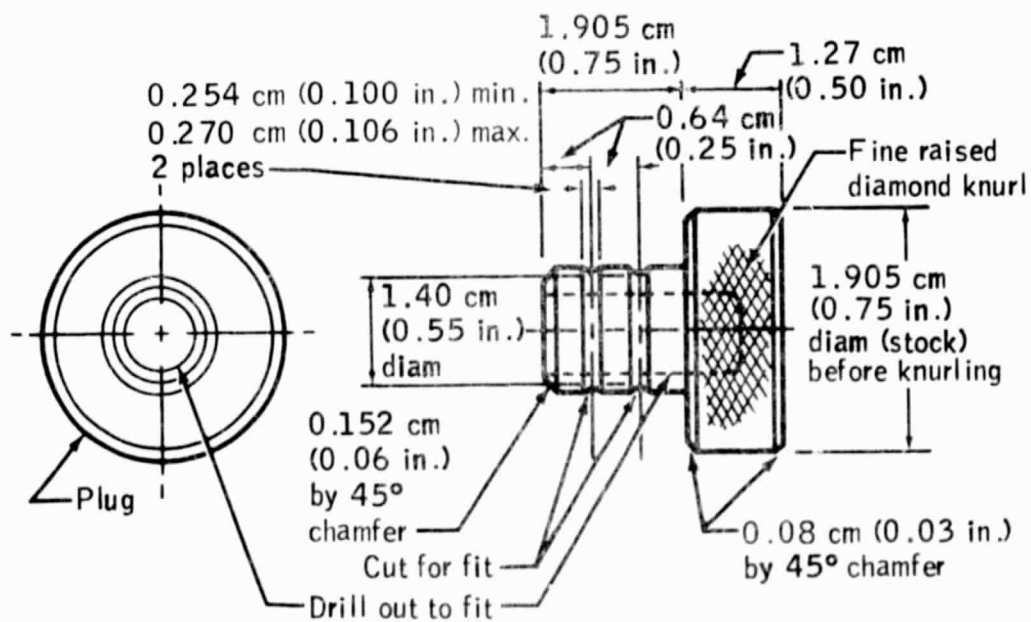


Figure 15.- Sample holder and access port.



(a) Quench port.



(b) Cap/cup for sealing port.

Figure 16.- Base plate for system.